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(54)【発明の名称】 非水電解液二次電池

(57)【特許請求の範囲】

【請求項 1】リチウム、リチウム合金またはリチウム化合物を負極、 $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$ (Me:Co、Cr、Ni、Ta、Znの中の少なくとも一種) で表わされる複合酸化物を活物質とする正極、リチウム塩を含む非水電解液、およびセパレータを有し、前記セパレータとしてあらかじめアルカリ水溶液に浸漬し、乾燥したものをを用いる非水電解液二次電池。

【請求項 2】セパレータの材料がポリオレフィンである請求項 1 記載の非水電解液二次電池。

【発明の詳細な説明】

産業上の利用分野

本発明は、非水電解液二次電池に関し、特にセパレータを改良した非水電解二次電池に関する。

従来の技術

リチウム、リチウム合金またはリチウム化合物を負極とする非水電解液二次電池は高電圧で高エネルギー密度となることが期待され、多くの研究が行なわれている。

特に、これら電池の正極活物質として MnO_2 や TiS_2 がよく検討されている。最近、タックレイらにより LiMn_2O_4 が正極活物質となることが報告された。(マテリアルリサーチ ブレチン1983年18巻461-472ページ) LiMn_2O_4 はスピネル構造をした立方晶の結晶構造であり、電池の正極活物質として用いた場合、電池の放電電圧は4ボルト程度の高い電圧となり、正極活物質として有望と考えられている。

$\text{Li}_x\text{Mn}_2\text{O}_4$ 正極活物質のX値と開路電位の関係を第4図に示す。4ボルト付近と2.8ボルト付近の2段の電位曲線となる。

ここで、高エネルギー密度を得るには、4.5ボルトま

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CLAIMS

(57) [Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery using what has the positive electrode which uses as an active material the multiple oxide expressed with a negative electrode and $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$ (at least a kind in Me:Co, and Cr, nickel, Ta and Zn) in a lithium, a lithium alloy, or a lithium compound, the nonaqueous electrolyte containing lithium salt, and a separator, was beforehand immersed in the alkali water solution as said separator, and was dried.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 whose ingredient of a separator is polyolefine.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

Field of the Invention Especially this invention relates to the nonaqueous electrolysis rechargeable battery which improved the separator about a nonaqueous electrolyte rechargeable battery.

Prior art It is expected that the nonaqueous electrolyte rechargeable battery which uses a lithium, a lithium alloy, or a lithium compound as a negative electrode will serve as a high energy consistency by the high voltage, and many researches are done.

Especially, MnO_2 and TiS_2 are well examined as positive active material of these cells. It was reported that LiMn_2O_4 serves as positive active material with tuck leis recently.

(461 - 472 pages of material research 1983 bulletins [18 volume]) LiMn_2O_4 is a cubic crystal structure which has Spinel structure, when it uses as positive active material of a cell, the discharge voltage of a cell turns into a high electrical potential difference of about 4 volts, and it is thought that it is promising as positive active material.

X value of 2OLiXMn_4 positive active material and the relation of open circuit potential are shown in Fig. 4 . It becomes two steps of potential curves, near 4 volt and near 2.8 volt.

It charges until the charge-and-discharge cycle which uses the 1st step in the potential curve which charges to 4.5 volts and discharges to 3 volts here in order to obtain a high energy consistency, i.e., X value, becomes 0.7 or less preferably one or less, and to discharge until X value is set to 1, or until it is set to 1.85 is desired. However, the cycle property of the 1st step of charge and discharge which charge until X value becomes 0.7 or less will be bad, and discharge capacity will fall to one half with about 50 cycle extent. Moreover, when extent to which X value exceeds 0.7 is charged, sufficient discharge capacity cannot be obtained.

Then, it is expressed with formula $\text{Li}_x\text{MYMn}_{2-y}\text{O}_4$, and it is a kind in Co, Cr, nickel, Ta, and Zn at least, and M is $0.85 \leq X \leq 1.15$, the amelioration using the positive active material which is $0.02 \leq Y \leq 0.3$ is made, and improvement in a cycle property is achieved.

Object of the Invention Although the large improvement in a cycle property was realizable by using the above-mentioned positive active material, in order that a charge

electrical potential difference might exceed 4V, there was a problem that the self-discharge property of the cell after charge was inadequate. About the self-discharge of a nonaqueous electrolyte rechargeable battery, disassembly of the minute amount moisture inside a cell or an electrolytic-solution solvent becomes a cause, and the problem of increase of cell internal resistance or the fall of charge-and-discharge capacity is caused. These phenomena become remarkable and will become more remarkable at the time of elevated-temperature maintenance, so that especially cell voltage becomes high. since [namely,] it becomes a high electrical potential difference by the time of charge in a 4V class lithium secondary battery -- electrical and electric equipment, such as disassembly of an electrolytic-solution solvent, and the reactivity of an electrode active material ingredient and the electrolytic solution, -- it is exposed to the condition that scientific activity is high. Therefore, there is a possibility that it cannot be adapted for a 4V class lithium secondary battery immediately in the conventional components including a separator.

Thus, I thought that a separator was in one of the conventional components with the need of inquiring. In the case of a nonaqueous electrolyte rechargeable battery, a separator is not invaded by the organic solvent excluding moisture, but satisfies the still more nearly required electrical property at the time of cell use, and a cheap thing is searched for. Polyolefine system resin is mainly used as a thing equipped with these requirements. Thus, efforts to contribute to the improvement in the engine performance of a lithium secondary battery also about a separator ingredient are made, and the self-discharge engine performance in the lithium secondary battery in which nominal-voltage 3V are shown has become what was very excellent. However, it is thought in the 4V class lithium secondary battery dealt with by this invention that there is room of the property amelioration.

About the moisture carried into the interior of a cell, efforts to suppress carrying in of moisture to the interior of a cell by the purification including distillation processing of the electrolytic solution, desiccation processing of positive active material, etc. are made. However, in the case of a rechargeable battery with the need of carrying out by repeating charge and discharge, when a charge electrical potential difference exceeds 4V especially, a good self-discharge property cannot be acquired only by removal of these moisture.

The reaction of positive active material and an electrolytic-solution solvent and the reaction of the matter and negative-electrode lithium which were generated by this reaction become easy to occur, and it is thought that the degradation of a cell arises. This invention solves such a technical problem and it aims at offering the nonaqueous electrolyte rechargeable battery which improved the self-discharge property, and its manufacturing method.

The means for solving a technical problem In order to solve this technical problem, in the nonaqueous electrolyte rechargeable battery which has the nonaqueous electrolyte and the separator containing the positive electrode which uses as an active material the multiple oxide expressed with a negative electrode and $\text{LiMn}_2\text{-XMeXO}_4$ (at least a kind in Me:Co, and Cr, nickel, Ta and Zn) in a lithium, a lithium alloy, or a lithium compound, and lithium salt, what was beforehand immersed in the alkali water solution and dried said separator is used for the nonaqueous electrolyte rechargeable battery of this invention.

Moreover, as for said separator ingredient, it is desirable that it is polyolefine system resin.

Operation The nonaqueous electrolyte rechargeable battery of this invention and its manufacturing method can obtain the 4.0V class nonaqueous electrolyte rechargeable battery excellent in the self-discharge property by this configuration. Although work of the alkali treatment of the separator in the interior of a nonaqueous electrolyte rechargeable battery is not clear, as the operation, control of disassembly of the organic electrolytic solution, a reaction with a decomposition product, etc. can be mentioned. Consequently, a solvent decomposition product is considered that the cell performance degradation considered to be the cause is mitigable.

Example The nonaqueous electrolyte rechargeable battery of one example of this invention and its manufacturing method are explained based on a drawing below.

(Example 1)

Manufacture of a cell is performed as follows. namely, -- as positive active material -- 0.204100g of $\text{LiMn}_{1.8}\text{Co}$ (es) -- as an electric conduction agent -- acetylene black 3.0g -- mixing -- this mixture -- 80 degrees C -- 10 hours -- drying -- 4.0g of Pori 4 fluoridation ethylene resin as after that and a binder -- mixing -- a positive electrode -- it considered as the mixture. a positive electrode -- 1t /carried out press molding by 2 cm, and 0.1g of mixtures was used as the positive electrode at the diameter of 17.5mm. The sectional view of a cell which manufactured is shown in Fig. 3 . The cast positive electrode 1 is put on a case 2.

Next, the porous polypropylene film was beforehand immersed at 30 degrees C as an alkali-metal hydroxide as a separator for 1 hour into the water solution of the 0.15-mol [l.] concentration of lithium-hydroxide LiOH . It took out after that, fully rinsed with ion exchange water, and was made to dry at 80 degrees C for 10 hours.

Thus, the obtained separator 3 was placed on the positive electrode 1. The with a diameter thickness [0.3mm thickness of 17 or 5mm] lithium plate was stuck to the obturation plate 5 which attached the gasket 6 made from polypropylene by pressure as a negative electrode 4. As nonaqueous electrolyte, this was added on the separator 3 and the negative electrode 4 using the propylene carbonate solution which dissolved one mol [l.] lithium perchlorate. The cell was obturated after that. The cell obtained as mentioned above is set to A.

The cell using the separator which was immersed in the potassium-hydroxide KOH water solution, and was dried by the same approach B, The cell using the separator which was immersed in the sodium-hydroxide NaOH water solution, and was dried C, It is immersed in a potassium hydroxide KOH and the mixed water solution (0.15-mol [l.] concentration) of sodium-hydroxide NaOH . The cell using the separator which was immersed in the mixed water solution (0.15-mol [l.] concentration) of D, lithium-hydroxide LiOH , potassium-hydroxide KOH , and sodium-hydroxide NaOH , and dried the cell using the dry separator is set to E.

The cell when it is not immersed in an alkali water solution but only desiccation performs a separator as an example of a comparison was constituted. This cell is set to F.

The self-discharge trial of a cell is performed by the following approach. Namely, about the cell obtained by the above-mentioned approach, it charged to 4.5 volts by 2mA constant current, and discharged to 3 volts, and after charge of 1 cycle eye finished this charge and discharge after 10 cycle *****, it stored for four weeks at 45 degrees C. It

discharged on the same conditions after storage. Here, the rate of self-discharge was defined as follows.

The rate of self-discharge = (discharge quantity of electricity of the discharge quantity of electricity-11 cycle eye of 10 cycle eye) discharge quantity of electricity of a /10 cycle eye Change of the cell internal resistance accompanying 45-degree-C preservation of each above-mentioned cell is shown in Fig. 1 .

Conventionally, by the cell F of a configuration, the increment rapid from immediately after preservation in cell internal resistance is accepted, and it is set to 40ohms or more after four weeks. The increment in cell internal resistance is [in / on the other hand / cell A-E of this example] very small.

Moreover, the rate of self-discharge four weeks after each cell is shown in the 1st table.

第 1 表

	電池A	電池B	電池C	電池D	電池E	電池F
自己放電率 (%)	0.09	0.10	0.02	0.05	0.06	0.42

Although Cell F is a very big rate of self-discharge, cell A-E of this example shows a good self-discharge property. Thus, it being beforehand immersed in an alkali water solution as a separator, and using the dry thing has the effectiveness which controls the self-discharge accompanying elevated-temperature preservation, and also when any of potassium-hydroxide KOH, a sodium hydroxide, and a lithium hydroxide are used as an alkali water solution, it is effective.

Furthermore, the same effectiveness is accepted also when these mixed water solutions are used.

(Example 2)

The nonwoven fabric made from polyethylene was used as a separator. This was beforehand immersed at 30 degrees C as an alkali-metal hydroxide for 1 hour into the water solution of the 0.15-mol [/l.] concentration of lithium-hydroxide LiOH. It took out after that, fully rinsed with ion exchange water, and was made to dry at 80 degrees C for 10 hours.

As positive active material, 0.2O4100g of LiMn1.8nickel was used. this active material -- as an electric conduction agent -- acetylene black 3.0g -- mixing -- this mixture -- 80 degrees C -- 10 hours -- drying -- after that -- 4.0g of Pori 4 fluoridation ethylene resin as a binder -- mixing -- a positive electrode -- it considered as the mixture. a positive electrode -- 1t /carried out press molding by 2 cm, and 0.1g of mixtures was used as the positive electrode at the diameter of 17.5mm. The sectional view of a cell which manufactured is shown in Fig. 3 . The cast positive electrode 1 is put on a case 2.

The separator 3 obtained as mentioned above was placed on the positive electrode 1. The with a diameter thickness [0.3mm thickness of 17 or 5mm] lithium plate was stuck to the obturation plate 5 which attached the gasket 6 made from polypropylene by pressure as a negative electrode 4. As nonaqueous electrolyte, this was added on the separator 3 and the negative electrode 4 using the propylene carbonate solution which dissolved one mol [/l.] lithium perchlorate. The cell was obturated after that. The cell obtained as mentioned above is set to 1.

The cell using the separator which was immersed in the potassium-hydroxide KOH water solution, and was dried by the same approach is immersed in 2 and a sodium-hydroxide NaOH water solution. The cell using the dry separator is immersed in 3, a potassium hydroxide KOH, and the mixed water solution (0.15-mol [l.] concentration) of sodium-hydroxide NaOH. The cell using the separator which was immersed in the mixed water solution (0.15-mol [l.] concentration) of 4, lithium-hydroxide LiOH, potassium-hydroxide KOH, and sodium-hydroxide NaOH, and dried the cell using the dry separator is set to 5.

The cell when it is not immersed in an alkali water solution but only desiccation performs a separator as an example of a comparison was constituted. This cell is set to 6.

The self-discharge trial of a cell was performed on the same conditions as an example 1. Change of the cell internal resistance accompanying 45-degree-C preservation of each above-mentioned cell is shown in Fig. 2 .

Conventionally, by the cell 6 of a configuration, the increment in cell internal resistance is remarkable, and is set to 40ohms or more after four weeks. On the other hand, in the cells 1-5 of this example, the increment in cell internal resistance is very small, and is the small cell of degradation.

Moreover, the rate of self-discharge four weeks after each cell is shown in the 2nd table. Although a cell 6 is a very big rate of self-discharge, the cells 1-5 of this example show a good self-discharge property.

第 2 表

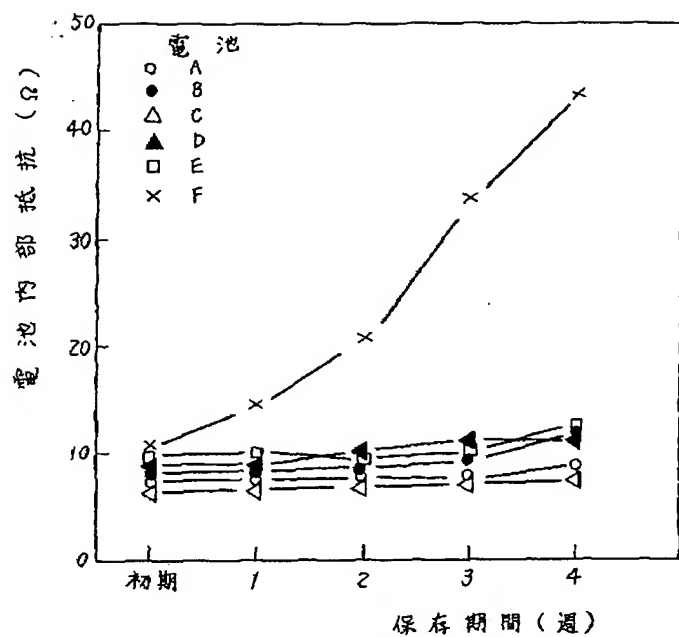
	電池1	電池2	電池3	電池4	電池5	電池6
自己放電率 (%)	0.08	0.05	0.07	0.10	0.09	0.35

Moreover, the same effectiveness was accepted also when $\text{LiMn}_{1.8}\text{nickel}_{0.2}\text{O}_4$, $\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$, $\text{LiMn}_{1.8}\text{Ta}_{0.2}\text{O}_4$, and $\text{LiMn}_{1.8}\text{Zn}_{0.2}\text{O}_4\text{Co}$ were used as positive active material.

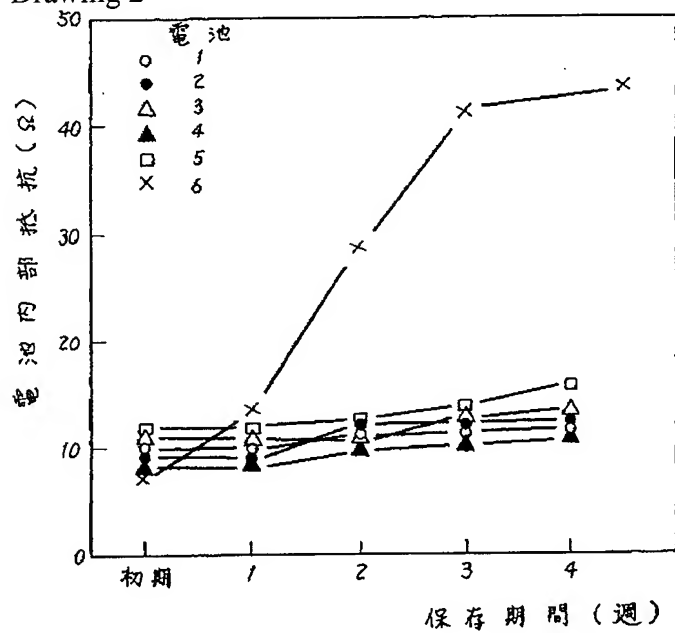
Furthermore, although the above-mentioned example showed porous polypropylene or a polyethylene nonwoven fabric as a separator, also when porous polyethylene and nonwoven fabric polypropylene are used, it cannot be overemphasized that there is same effectiveness.

Effect of the invention By explanation of the above example, according to the nonaqueous electrolyte rechargeable battery of this invention, and its manufacturing method, so that clearly They are a negative electrode and $\text{LiMn}_2\text{-XMeXO}_4$ (Me:Co) about a lithium, a lithium alloy, or a lithium compound. The positive electrode which uses as an active material the multiple oxide in Cr, nickel, Ta, and Zn expressed with a kind at least, By having the nonaqueous electrolyte containing lithium salt, and a separator, being beforehand immersed in an alkali water solution as said separator, and using the dry thing, a self-discharge property can obtain a good nonaqueous electrolyte rechargeable battery, and the meaning on industry has it. [large]

Drawing 1

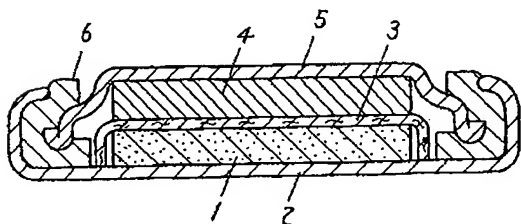


Drawing 2



Drawing 3

1 --- 正 極
4 --- リチウム板



Drawing 4

